

Ni-doped versus undoped Mg–MgH₂ materials for high temperature heat or hydrogen storage

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Abstract

A comparative study of the behavior of various Ni-doped and undoped Mg–MgH₂ materials to be utilized for reversible (thermochemical) high temperature heat or hydrogen storage has for the first time been conducted over a broad range of hydrogenation/dehydrogenation (cycling) conditions (see Fig. 5). The storage capacity losses observed in the course of cyclic tests are found to be sensitively dependent to all the details of the applied cycling conditions and can be of temporary (reversible) or persistent (irreversible) nature. Based upon investigations via optical microscopy, the reversible capacity losses appear to be associated with an excessively high formation rate of MgH₂-nucleation sites on the surface of Ni-doped Mg particles under intensified cycling conditions; irreversible capacity losses, especially pronounced in the case of Ni-doped materials, are the result of sintering of the material particles in the dehydrogenated (metallic) form upon prolonged cycling at higher temperatures.

Ni-doped Mg–MgH₂ materials have excellent cyclic stability and high hydrogenation rates even under very mild pressure/temperature cycling conditions (so-called standard cycling conditions or below them [B. Bogdanović, Th. Hartwig, B. Spliethoff, Int. J. Hydrogen Energy 18 (1993) 575; Final Report of Project No. 0328939 C, Federal Ministry for Research and Technology of the F.R.G., Bonn (1992)]) suitable for applications such as solar generation of heat and cold, heat pumps, hydrogen storage, and the like. On the other hand, based on their cyclic stability and sufficient reaction rates under severe reaction conditions, neat Mg powders produced by brushing can be used as cheap materials for the purpose of reversible thermochemical high temperature heat storage in the temperature range of 450–500°C with heat storage capacities amounting to 0.6–0.7 kWh/kg Mg, applicable for solar power generation via Stirling engines or storage of industrial heat in the above temperature ranges. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

In 1993, a systematic study was published [1,2] dealing with the applicability of various Ni-doped and undoped Mg powders as materials for reversible thermochemical heat [3] or hydrogen [3–7] storage. For this purpose, the materials were subjected to a series of hydrogenation/dehydrogenation cycles (cycling tests) under different operating conditions, while rates and extent of hydrogen charging and discharging processes during hundreds of cycles were monitored. A remarkable result stemming from that study [1,2] is the behavioral contrast of Ni-doped versus undoped Mg materials with respect to losses in

hydrogen capacity: the major capacity losses were found to take place with Ni-doped materials during cycling under severe temperature and pressure conditions while, on the other hand, undoped Mg powders showed relatively high cyclic stability under such conditions.

One of the objectives of the present study was to obtain detailed information about the nature and causes of hydrogen capacity losses during cycle tests and to discover operational conditions under which these can be minimized. In this connection, morphological investigations of Ni-doped and undoped Mg materials in the course of cyclic tests have been carried out.

As the final goal of our work along these lines, we envision the development of a Mg–MgH₂ based thermochemical heat storage material with satisfying cyclic stability and heat capacity and a heat discharge temperature ap-

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proaching or exceeding the $\sim 500^\circ\text{C}$ temperature level (see also the Mg–Fe hydride system, Refs. [8,9]). This temperature is considered to be a compromise between, on the one hand, the goal of attaining high (Carnot) efficiencies of thermal (thermodynamic) machines such as Stirling engines [1,2,10–15] and the like, driven by the thermochemical heat store and, on the other hand, the necessity of avoiding technical material problems connected with the construction and operation of high temperature and high hydrogen pressure heat storage vessels. This means, for example, that when using the MgH_2 –Mg system, the 500°C heat discharge temperature requires hydrogenation pressures of not less than (or above) 100 bar (see. Fig. 5 [16] and Section 3.5).

2. Experimental part

The *standard test* (Sections 3.2 and 3.3, Figs. 2 and 3) was described earlier [1,2] detailed description in [14]; volume of the H_2 pressure cylinder used: 5 l.

The *survey test* (Section 3.4) was carried out using a commercially purchased equipment of HWT company (Hydrid–Wasserstoff–Technik, Mülheim an der Ruhr, Germany). The apparatus operates on the same principle as does the standard test apparatus (see above); however, it can reach temperatures of up to 500°C under 100 bar of H_2 pressure, and furthermore, it enables simultaneous and independent measurements on three different samples [1,2], detailed description in [14]. The autoclaves (40 ml of volume) of the equipment are constructed in the same way as that of the standard test apparatus, except that stronger screws were used. Volume of the H_2 pressure cylinder: 1 l. Amount of storage materials investigated in each one of the autoclaves: ~ 20 g. The complete equipment was made air-free by means of multiple evacuations and charging with H_2 and placing under 25 bar of H_2 . The autoclaves were then heated to 350°C . Hydrogenation of the Ni-doped standard material begins already during the heating-up period ($\sim 180^\circ\text{C}$), and after 2 h, 90% of the total amount of hydrogen taken up during the first hydrogenation (6.53 wt.%) was absorbed. Hydrogenation of the undoped and mechanically Ni-doped 270 mesh Mg powder (Eckart–Werke (5 wt.% Ni)) only begins about 4 h after the 350°C temperature level has been reached and is much slower, cf [1,2] and [14]. Hydrogenation of all three samples was completed in 24 h (the H_2 pressure drops during this time to 10 bar). They were then quantitatively dehydrogenated within 1 h at 440°C , whereby again the initial H_2 pressure of 25–26 bar was attained. The survey test is described further in Section 3.4 and represented graphically in Fig. 4.

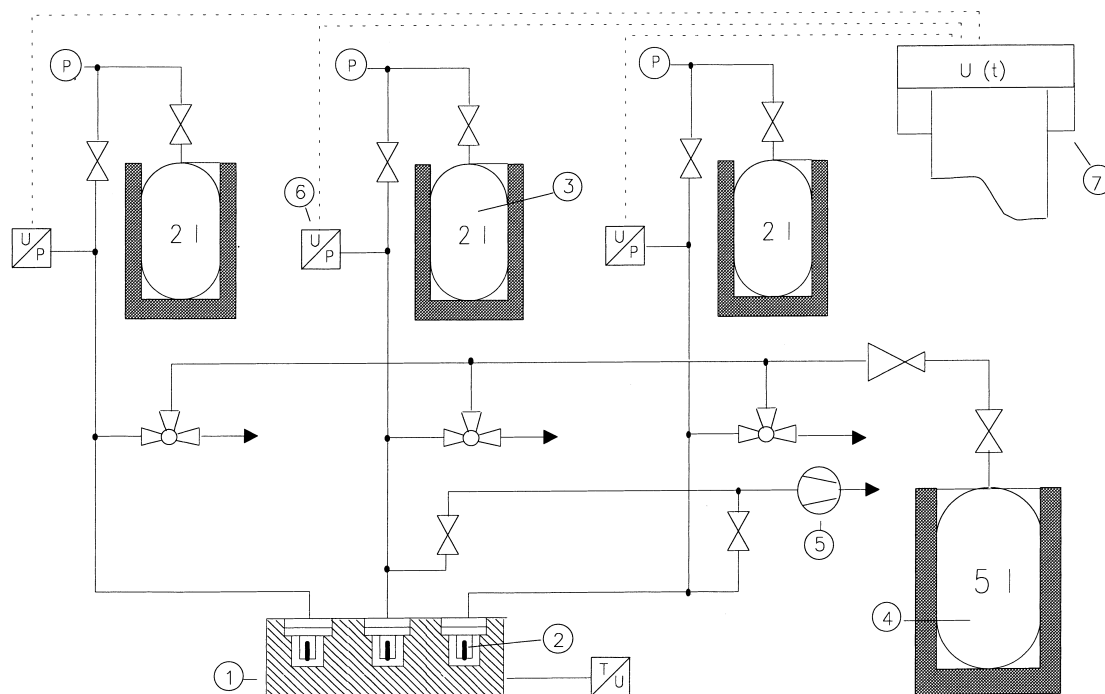
Removal and preparation of samples for light microscopy (Figs. 6 and 7) was performed under Ar atmosphere. Different Mg or MgH_2 samples placed in a dish were mixed in the 1:1 ratio with a transparent 2-component embedding agent with an acrylate base (Mounting Resin 3)

and then covered with an excess amount of the latter. The samples were then pressed inside a heatable press (Pron-topress 2, Struers Co) in the course of 5 min at 180°C (MgH_2 : 18 kN/4 cm^2 ; Mg: 25 kN/4 cm^2). The pressed samples were first ground by means of a grinding wheel with abrasive paper (800 $\rightarrow$ 1000 $\rightarrow$ 4000) and then polished with a felt polishing disc with diamond pastes of 3.1 and 0.25 μm grain sizes. For both grinding and polishing, ethanol was used as a lubricant. For MgH_2 containing materials, the polishing rate must be kept low (1500 r.p.m.), in order to not remove hydride particles from the embedded material thus scratching the polished samples. In addition, the polishing time must be kept short (~ 2 min), because too long a contact-period with the lubricant (ethanol) could cause the surface of polished cuts to corrode. For the same reason, after polishing, the samples must be dried as rapid as possible.

High temperature cycling tests (Section 3.5): For conducting the tests at hydrogenation pressures and temperatures of up to 100 bar/ 470°C (Fig. 9a,c; first series of HT cycling tests), the above mentioned HWT equipment was used. For performing the HT cycle tests in hydrogenation pressure and temperature ranges from 100/ 470 to 140 bar/ 515°C (Figs. 9b,d and 10a,b; second and third series of HT cycling tests), a new piece of equipment (Fig. 1) was built. This equipment differs from the HWT equipment in that the heat resistant steel 1.4980 (27.2% Ni, 16.2% Cr, rest Fe) for the autoclaves (36 ml volume) and a 2 l H_2 pressure cylinders (instead of 1 l) were being used. In the third series of HT cycling tests (Fig. 10a,b) autoclaves were used of the type represented in Fig. 1b, which were designed for 150 bar/ 550°C (stretch screws were made of 1.7711, CrMoV47 material); the autoclaves of Fig. 1b are constructed in such a way to enable the installation of a sinter tube (for supply of H_2) and/or a thermocouple; the latter can be inserted in the Mg– MgH_2 bed, thus measuring the inner temperature of samples in the course of cycling tests (see Fig. 10). In order to protect the storage materials from contamination with products of degradation of autoclave walls, the autoclaves were equipped with cylindrical steel inserts (steel 1.0037, 99% Fe, 0.17% C).

The particle size distribution of the four different samples of Mg powder was determined by using analysis sieves DIN 4188. Separations of 20 g amounts of each sample (30 min of sieving on an automatic shaking stand and 3 min of manual sieving) were repeated three times, giving reproducible results, the average results of which are given in Fig. 8. The Ni-doped samples are based on the Mg powder PK-31 (Eckart–Werke) and are thus of comparable particle size distribution to this Mg powder.

In the first and second series of the HT cycling tests (Fig. 9), the charging of the autoclaves with the Mg powder samples took place by shaking the autoclaves on an automatic shaker. In this way, the maximum amount of materials in the 36 ml volume of the autoclaves can be reached without any additional mechanical pressure. This



a

Fig. 1. (a) Schematic representation of the equipment used for conducting high temperature cycling tests: ①, Al-block with heating cartridges; ②, autoclave, see Fig. 1b); ③, 2 l H₂ pressure cylinder; ④, 5 l H₂ stock pressure cylinder; ⑤, vacuum pump; ⑥, pressure–tension transformer; ⑦, 4 channel recorders. (b) drawing of the 36 ml volume autoclave (in mm).

method is recommended for charging the autoclaves with storage materials, since no detrimental influence on the storage properties was observed (cf. maximum of filling density of Mg–MgH₂ storage materials in Refs. [17–19]). Under these conditions the filling densities and porosities of Mg powders ($p_{\text{Mg}} = 1.74 \text{ g/cm}^3$) as given in Table 1 can be achieved.

In the third series of HT cycling tests (Fig. 10) the amounts of Mg powder used were 20.0 g each.

3. Results and discussion

3.1. Materials and methods

For the purpose of fixing and comparing properties of various kinds of Ni-doped and undoped Mg–MgH₂ materials as heat (or hydrogen) stores [20], in the previous study [1,2], the so-called *standard (storage) material* and the *standard cycling test* (Section 3.2), were defined.

As *standard material* has been designated a 270 mesh Mg powder (Eckart–Werke) of known particle size distribution (Fig. 8), produced by mechanical metal-cutting (brushing) of bulk magnesium and doped with 2 wt.% of Ni according to a *standard procedure* (bis[1,5-cyclo-octadiene]nickel as a doping agent) [1,2]. The standard

material has successfully been tested as a heat storage medium in a laboratory demonstration unit for the generation of superheated steam [10,11] in a heat store unit designed to be used for driving a Stirling engine [12,13] and in a compound system with a low temperature hydride store for simultaneous generation of heat and cold [10,11,21,22]. The last two applications were designed to be operated in solar systems. Thermodynamic [6,7,16], heat conductivity [10,11,23,24], compressibility [17,19] and “ignition temperature” properties [6,7] as well as the long-term cyclic stability tests [25] of the standard material have also been investigated.

In continuation of the study of Mg–MgH₂ storage materials it has been shown [1,2] that the simplest and by far the least expensive method for the preparation of Ni-doped materials is the *mechanical mixing* of Mg powder with a few wt.% of fine Ni powder in dry state. The thus prepared materials revealed, besides storage properties close to those of the standard material, the highest yet observed cyclic stability in long-term standard tests [1,2,26].

In the present study, the behavior of standard and mechanically Ni-doped materials as well as of undoped Mg powders is being investigated in the course of standard (Section 3.2), survey (Section 3.4), and high temperature tests (Section 3.5).

Table 1

Filling densities and porosities achieved by charging the autoclaves (volume 40 ml) with Mg powder used throughout the high temperature cycling tests

Mg powder	Weight of Mg powder [g]	Filling density [g/ml]	Porosity [%]
NH sample	32.00	0.80	54
PK-31 sample	31.15	0.78	55
325 mesh	29.62	0.74	57
Ar-sprayed	40.6	1.00	42
Standard material	33.97	0.85	51

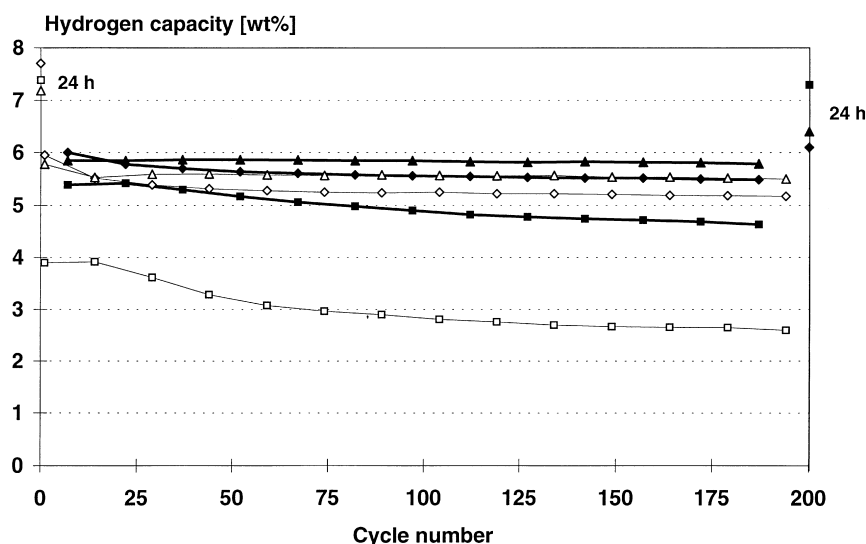


Fig. 2. Dependence of the hydrogen storage capacity upon the number of cycles for the standard cycling test: —△—, —▲—, standard Ni-doped material; —□—, —■—, 270 mesh Mg powder (Eckart-Werke); —◇—, —◆—, foregoing Mg powder, mechanically doped with 5 wt.% of Ni powder; blank and filled symbols represent hydrogenation times of 45 and 135 min, respectively.

decrease. By returning to scc (Section 3) the cycling stability can be restored but at a slightly lower level. After both the temperature and pressure of dehydrogenation have been raised considerably (Section 4), the return to scc

(Section 5) brings about a rapid recovery of storage capacity but now at a considerably lower level.

From this example can be concluded that the H_2 capacity losses occurring under intensified cycling con-

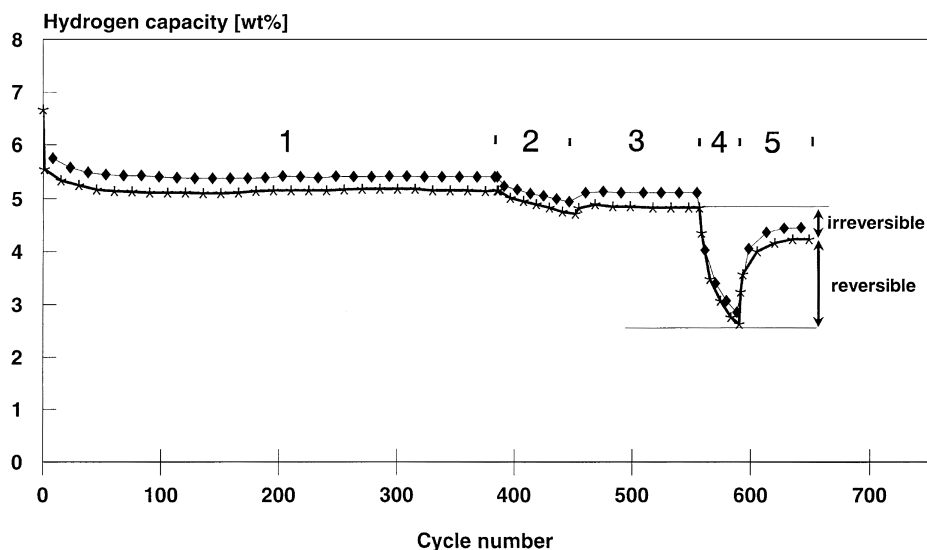


Fig. 3. A 700 cycles test performed with mechanically Ni-doped (4 wt.%) 270 mesh Mg powder (Eckart-Werke), demonstrating reversible and irreversible hydrogen capacity losses; —*— and —◆—, 45 and 135 min hydrogenation times, respectively.

ditions can partially be reversed by switching to milder conditions (reversible capacity losses). Capacity losses which are not regained when turning to initial, more moderate conditions can accordingly be designated as *irreversible* ones.

Knowledge of the described phenomena is of practical importance for the operation of Mg–MgH₂ based heat or hydrogen stores. It was, therefore, of considerable interest to try to elucidate their underlying physico–chemical mechanism (Section 3.4.2).

3.4. The survey (cycling) test

3.4.1. Cyclization conditions and results

The so-called survey (cycling) test was devised and carried out with the following intentions:

1. To achieve cyclic stability at a heat discharge temperature considerably higher than under standard conditions (cf. Introduction) and
2. To gain an insight into the possible causes for reversible and irreversible hydrogen capacity losses for both Ni-doped and undoped materials (cf. Section 3.3).

Accordingly, samples of the standard and mechanically Ni-doped materials and of the undoped Mg powder were subjected to a test lasting 238 cycles simultaneously and under identical conditions (cf. Experimental section) during which the hydrogenation and dehydrogenation temperature and pressure were raised stepwise (Fig. 4). The chosen hydrogenation/dehydrogenation conditions cover a broad temperature/pressure range in the MgH₂–Mg diagram of state, as shown by ◯—○ in Fig. 5. The hydrogenations (Fig. 4) were carried out during a short period (1 h; simulation of a heat pump operation) or a long-term hydrogenation period (5 h; simulation of a heat store operation). For dehydrogenations 1 h was invariably allotted. During long-term hydrogenation cycles, the autoclave was cooled down from dehydrogenation to hydrogenation temperatures according to a temperature program exemplified in Fig. 4c (---) which is devised in such a way that the hydrogenation reaction proceeds in the vicinity of equilibrium conditions (simulation of a solar heat store operation [12,13,22]). At the end and at some characteristic moments of the test (marked by 6b,c and 7a–d in Fig. 4), samples of the materials [28] were removed from the autoclaves and investigated by means of microscopy (LM; Section 3.4.2).

During the first part of the survey test (Fig. 4a, cycle numbers 1–132) the hydrogenation pressure was raised from the initial 25 (360°C) [29] to 35 bar (360°C), and thereafter hydrogenation pressure and temperature were increased to 45 bar (400°C); at the end of the first part of the survey test, reaction conditions were once again turned to initial values (25 bar (360°C)). During each of the cycling periods with constant temperature and pressure

(Fig. 4), the short-term hydrogenation cycles were followed by long-termed ones.

As can be seen in Fig. 4a, the undoped and the Ni-doped Mg–MgH₂ materials differ profoundly from each other when cycled alternately under short- and long-term hydrogenation conditions: while the capacity of the undoped Mg powder (Fig. 4) remains at a high level under both conditions (5.5–6.7 wt.%), the Ni-doped materials under short-term hydrogenation conditions undergo a rapid and an increasing loss of hydrogen storage capacity (Fig. 4, —▲—, —◆—). The initial storage capacity, however, can be even more rapidly restored by switching to long-term conditions. Here, we are obviously dealing with *reversible* capacity losses. The recorded courses of cycles under short- and long-term hydrogenation conditions performed with the standard material are reproduced in Fig. 4b and c, respectively. The hydrogenation reaction under short-term conditions (Fig. 4b) progresses at first rapidly but the rate of H₂ absorption suddenly drops, well before the theoretical hydrogen capacity has been achieved. The bend in the hydrogenation curve is reached earlier and earlier with each single cycle, so that during a period of 21 cycles, the capacity continually decreases from 5.4 to 4.1 wt.% H₂. Under the long-term hydrogenation conditions (Fig. 4c; temperature controlled cooling, ---) no such capacity decrease is observed. As can be seen in Fig. 4a, all of the investigated materials reach, under long-term conditions throughout the entire survey test, higher storage capacities than under short-term hydrogen conditions.

In the second part of the test (Fig. 4; cycle numbers 133–238), with increasing hydrogenation pressure and temperature, both types of materials show a steady decrease in capacity which is more pronounced in the case of Ni-doped materials; these capacity losses (cf. to next section) are considered to be of *irreversible* type.

A general view of the survey test (Fig. 4a) shows that throughout the test the capacity curve of the undoped Mg powder (■) runs well above those of both Ni-doped materials (—▲—, —◆—). This contrasts highly with the behavior of the same materials during the standard test (Fig. 2), in which the capacity of the undoped Mg powder is considerably lower than that of the Ni-doped ones.

From these qualitative observations can be concluded that under operational conditions of the survey cycling test, the storage properties of the undoped Mg powder – the storage capacity and the cyclic stability – are superior to those of Ni-doped materials; at the end of the survey test, the capacity of the Mg powder can even be twice as high as that of the standard material. The application of the Ni-doped Mg powder in place of the same undoped Mg powder under the whole range of operational conditions of the survey test also brings no advantages with respect to the hydrogen absorption rate. The advantage of the Ni-doped Mg powder as an energy storage material emerges more clearly under the operational conditions of low pressures and temperatures, which are indispensable for

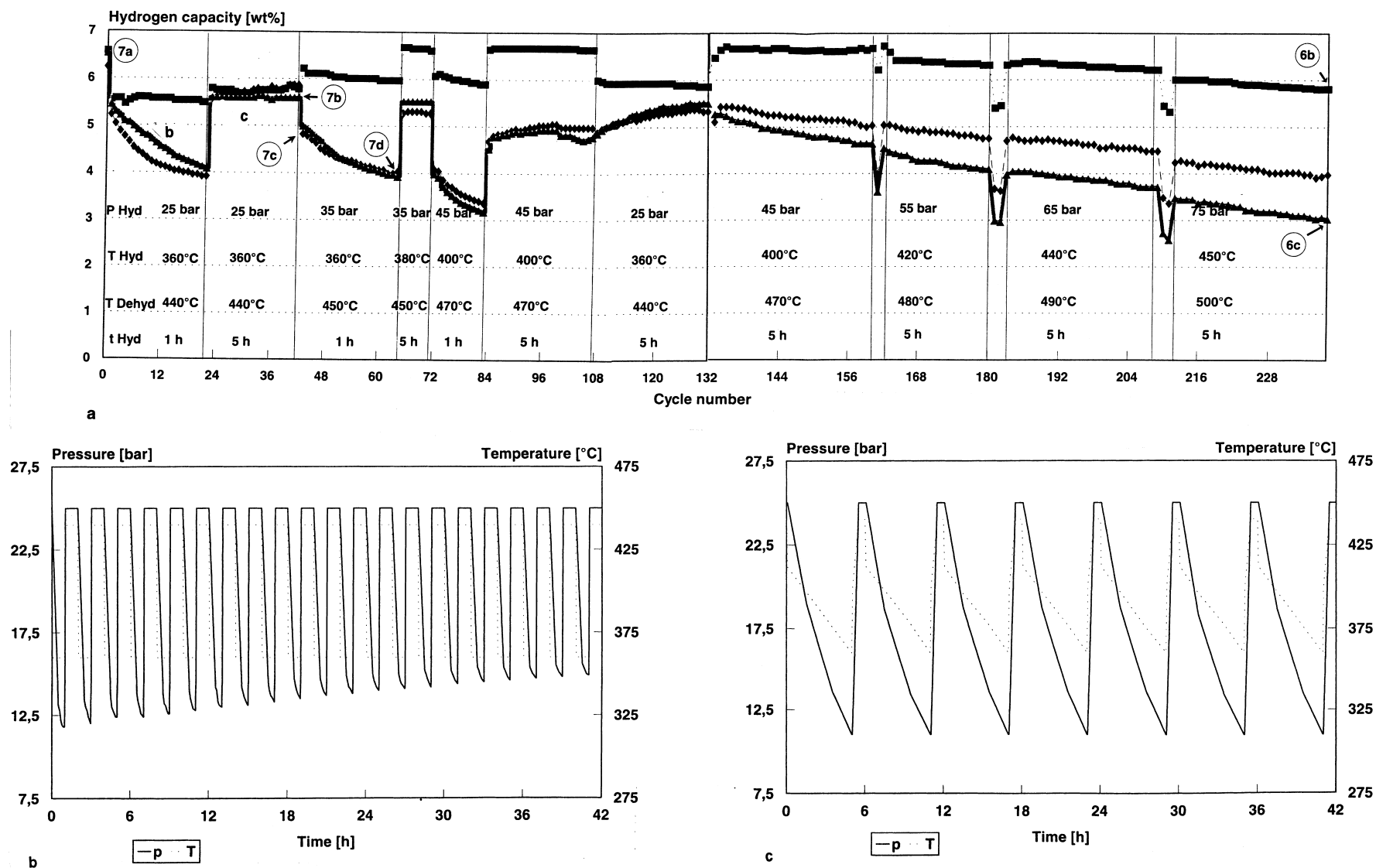


Fig. 4. (a) The survey cycling test performed simultaneously with standard material (—▲—), 270 mesh Mg powder (Eckart-Werke; ■) and mechanically Ni-doped (5 wt.%) foregoing Mg powder (—◆—); P_{Hyd} , initial hydrogenation pressure; T_{Hyd} , hydrogenation (oven) temperature; t_{Hyd} , time allotted for hydrogenation; T_{Dehyd} , dehydrogenation (oven) temperature; the final hydrogenation pressure (P_{Deh}) can be calculated by means of the relation that 1 wt.% of hydrogen capacity in 4a,b corresponds to a drop of hydrogen pressure in the system of 2.5 bar; ⑥b, ⑥c, ⑦a–d denotes points of removal of samples from the autoclaves in hydrogenated or dehydrogenated state, to be investigated via light microscopy (Figs. 6 and 7). (b) Portion of the chart recording the first 21 cycles of the survey test (a) performed with the standard material under short-term hydrogenation conditions; —, H_2 pressure [bar]; ----, oven temperature [°C]. (c) Portion of the chart recording 24–31 cycles of the survey test (a) performed with the standard material under long-term (temperature programmed) cooling conditions; —, H_2 pressure [bar]; ----, oven temperature, [°C].

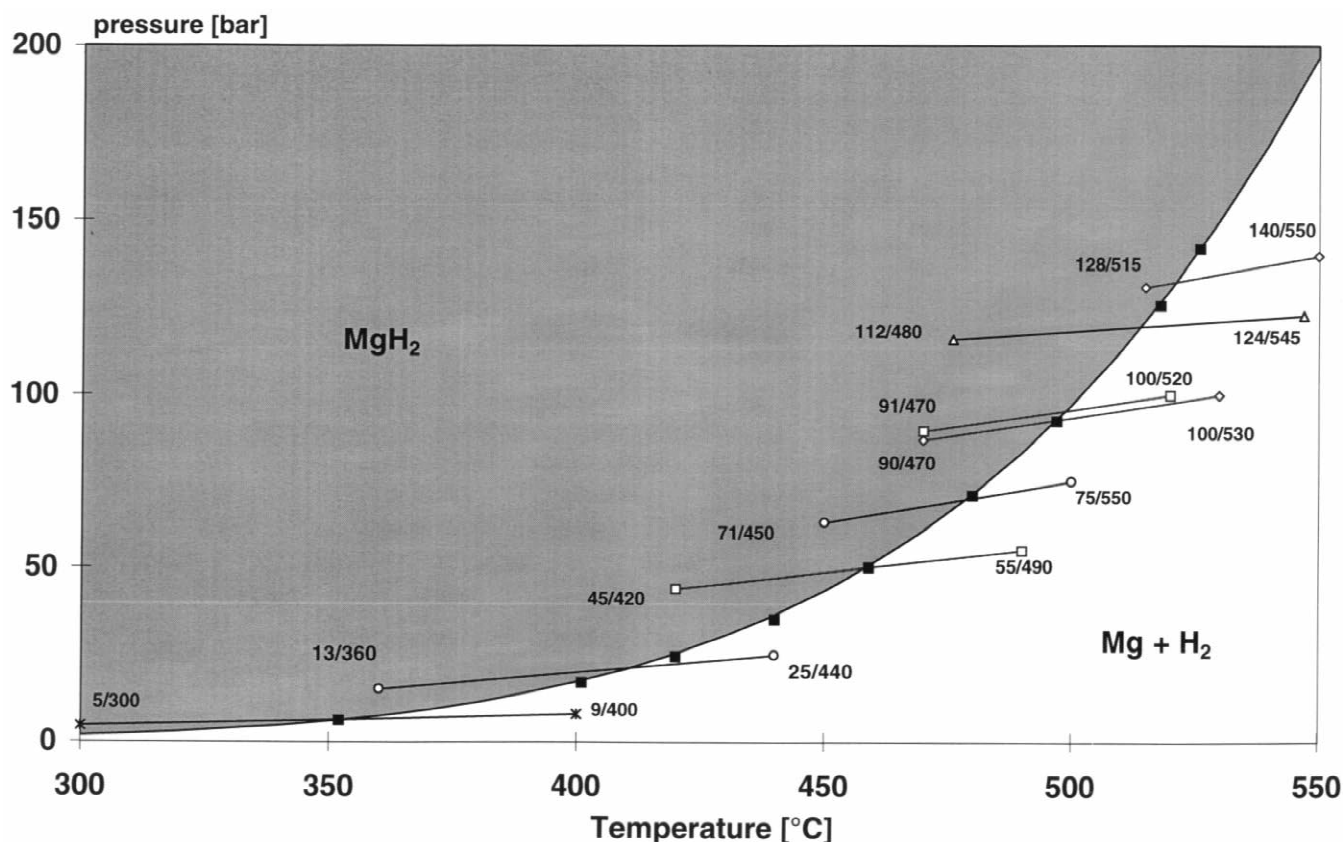


Fig. 5. Diagram showing experimentally determined (—■—, point of measurement) dependence of the equilibrium hydrogen pressure in the $\text{MgH}_2 \leftrightarrow \text{Mg} + \text{H}_2$ system (in bar) upon temperature (according to [16]); the “bars” in the diagram represent pressure and temperature ranges [bar/°C] of the standard (*—*; Fig. 2) and survey cycling tests (○—○; Fig. 4a) and of the first (□—□; Fig. 9a), second (◇—◇; Fig. 9b) and third series (△—△; Fig. 10a) of the high-temperature cycling tests.

example, for the simultaneous generation of heat and cold [10,11,21,22] and for hydrogen storage [3–7].

In this connection, it should be pointed out that the irreversible capacity losses occurring at higher temperatures (sintering) are the results of morphological and structural changes (cf. Sections 3.4.2 and 3.5) of the materials in *dehydrogenated state*. In order to minimize irreversible capacity losses during operation, exposure of the materials to higher temperatures in the discharged (metallic) form should be avoided as much as possible.

3.4.2. Morphological and structural changes of the storage materials occurring throughout the survey test

Fig. 6a and b show LM images of polished cuts of undoped Mg particles before and after (sample ⑥b in Fig. 4a) the survey test, respectively. After the test, the size of the Mg particles remained roughly the same, but the original shavings were reshaped into rather globular particles. In contrast to this, the particles of the Ni-doped standard material after the test (sample ⑥c in Fig. 4) were not only reshaped but also considerably enlarged (cf. Fig. 6b and c) [30].

The globulization and growth of the Mg particles in the

course of the survey test (Fig. 6b and c) occur via sinter processes [31]. Similar conclusions were reached previously by Akiba et al. [32] and Song [33]. The rate of the sintering processes is mainly determined by the temperature and the magnitude of the temperature dependent coefficient of (inter)diffusion of the corresponding materials. The diffusion laws [31] call for a high increase in the diffusion coefficient of a solid material near its melting point.

The fact that the operational temperatures of the survey test (Figs. 4 and 5) are in the same temperature range as the Mg–Ni eutectic, which lies at 506°C [34], explains the greater sintering tendency of Ni-doped materials in comparison to undoped Mg powder (m.p. 650°C).

The more progressed stage of the sintering process of the Ni-doped materials versus undoped Mg (Fig. 6b and c) parallels the greater loss in H_2 capacity of the former in the course of the survey test (Fig. 4a). On the other hand, from our previous study [1,2] it is known that the H_2 capacity of the Ni-doped materials decreases with increase in their particle size. The globulization and the growth of Mg particles (Fig. 6b, c) with respect to the starting materials (Fig. 6a) is thus the cause for the continuous irreversible loss of H_2 storage capacity of both doped and

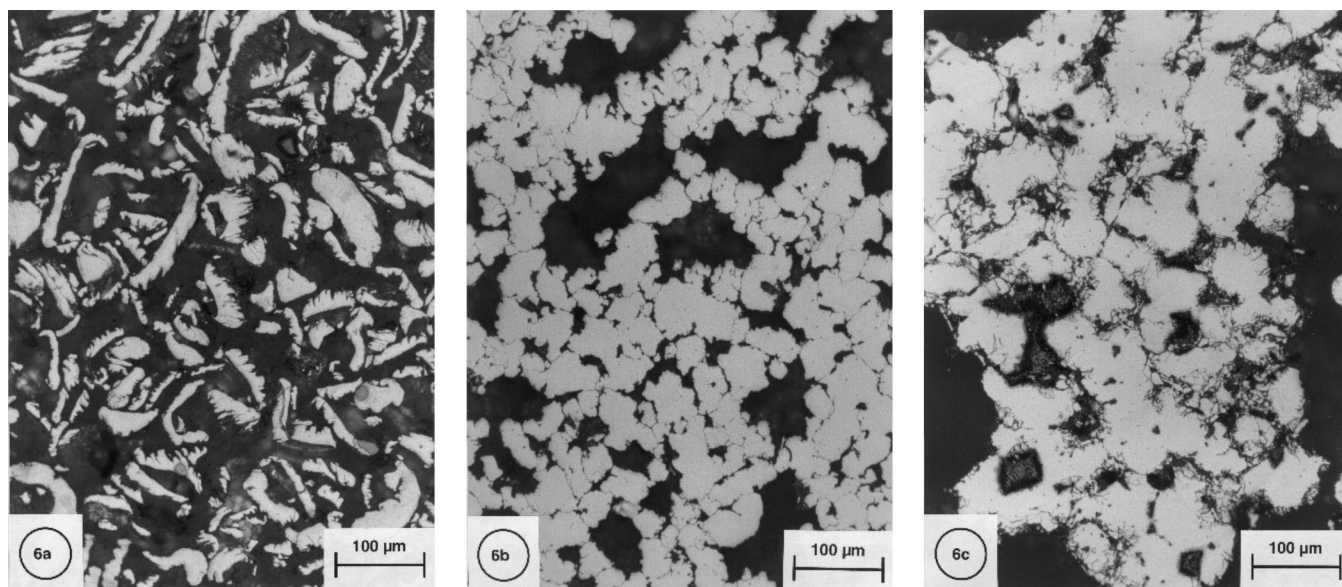


Fig. 6. (a) LM polished cut images of the 270 mesh Mg powder (Eckart–Werke) before the survey test; (b) after the survey test (sample 6b in Fig. 4a); (c) standard material in dehydrogenated state after the survey test (sample 6c in Fig. 4a).

undoped materials in the course of the survey test (Fig. 4a).

It is further known that the distribution of the sinter activator [31,35] (here Ni) on the surface of a material which is to be sintered (here Mg) is also a factor determining the rate of sintering. The more homogeneous distribution of Ni on the surface of Mg in the case of Ni-doped standard material, in comparison to the mechanically Ni-doped one, and its consequently more pronounced sintering, is thus the probable reason for its greater loss of H_2 capacity in the course of the survey test.

More complex and difficult to explain are the processes causing reversible capacity losses (Section 3.3). According to the generally accepted and experimentally confirmed mechanism [36–41], the hydrogenation of pure Mg takes place via a nucleation and growth process. Thereby, on the surface of Mg particles are created nucleation sites from which the reaction progresses spherically into the interior of the particle. As soon as the individual reaction fronts overlap each other, the reaction rate decreases drastically, because from now on, the rate is controlled by the extremely slow diffusion of hydrogen through the magnesium hydride layer [36–38]. Thus, the number of nucleation sites per particle should have a direct influence on the achievable extent of hydrogenation. In case of creating a vast number of nucleation sites, only a thin, dense MgH_2 layer will be formed on the surface of the Mg particles which is hardly permeable by hydrogen. According to the study on nearly spherical Mg powder particles, Vigeholm et al. [38,40] concluded that the nucleation rate increases with an increase in pressure and that the growth is controlled by hydrogen diffusion in the metal/hydride interface. The limited reaction observed at higher pressures is consistent with the proposed mechanism. As demon-

strated via SEM of cut sections of spherical particles, the number of nuclei increases and the depths of the MgH_2 layer and hence the maximum absorption decreases with an increase in the hydrogen pressure applied.

The nucleation and growth mechanism in the case of the *Ni-doped standard material* and pure Mg has been mathematically modelled and parallel kinetic measurements of the hydrogenation of the material have been performed. By appropriate choice of computational parameters, a good agreement between the model and measured curves was achieved, which can be taken as a confirmation of the validity of the nucleation and growth mechanism [42–44].

The validity of the nucleation and growth mechanism for the hydrogenation of Ni-doped standard material is further supported by a series of LM images which show polished cuts of the standard material in different phases of the survey test (Fig. 7) [14].

Fig. 7a shows the standard material after the *first* hydrogenation: besides the majority of completely hydrogenated Mg particles (grey), a partially hydrogenated example can be seen. The spherical growing zones of MgH_2 surrounding the Mg particle and their non-uniform penetration within the interior of the particle can be clearly discerned.

LM images of polished cut from a sample after a series of long-term hydrogenations are presented in Fig. 7b and, both after a few short-term hydrogenations and at the end of a series of such hydrogenations, exhibited in Figs. 7c and d. As can be seen in Fig. 7b–c, the decrease in capacity from 5.5 to 4 wt.% accompanying the series of short-term hydrogenations (Fig. 4a) clearly correlates with the diminishing depths of the hydride shell, up to only $\sim 2 \mu m$ at the end of the series (Fig. 7d). With the decrease in depths of the hydride shell (Fig. 7d), the number of

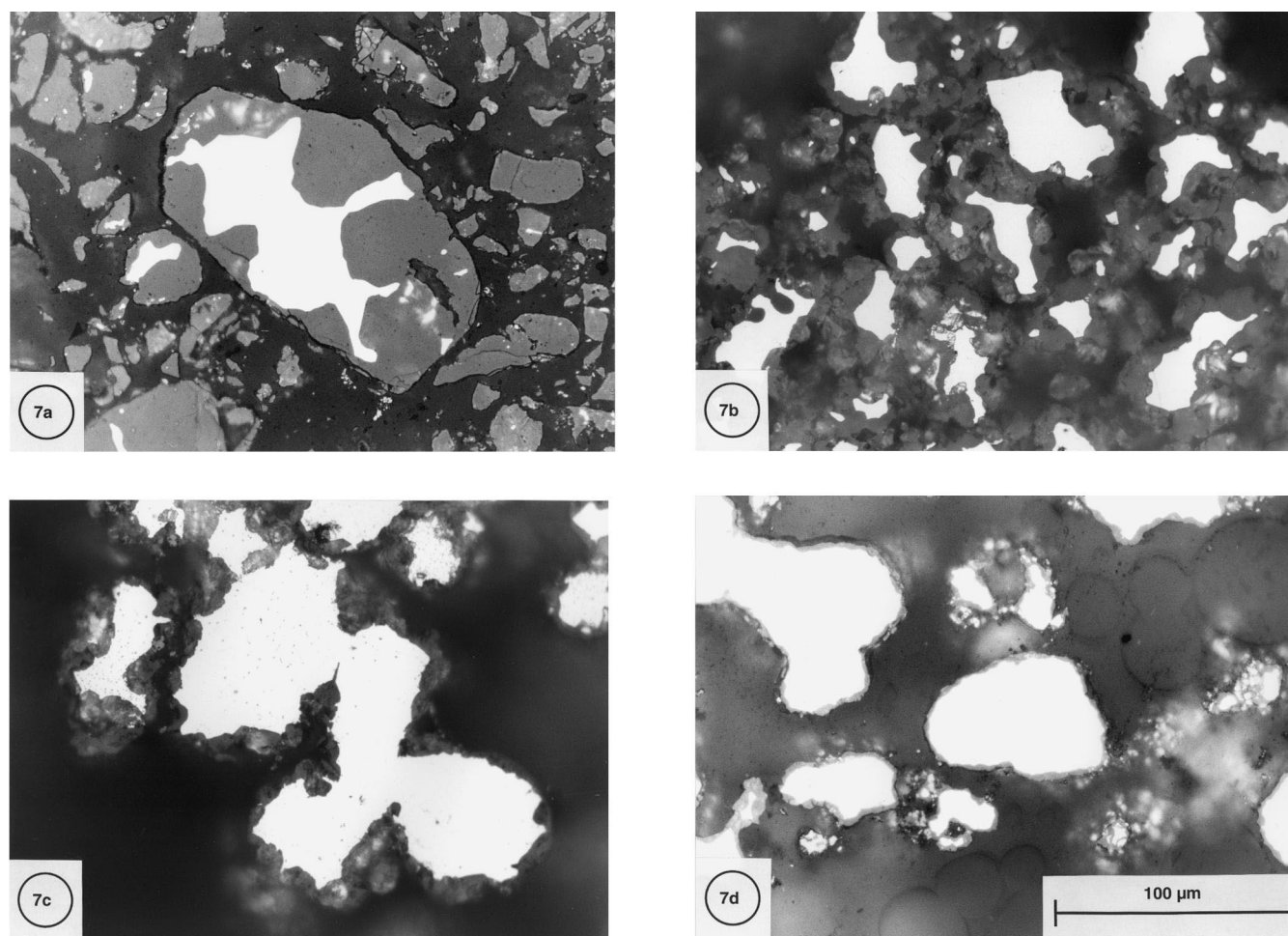


Fig. 7. LM polished cut images of the standard material Fig. 4a; 7a: after the first hydrogenation; 7b: after a series of long-term hydrogenations; 7c: after a few short-term hydrogenations; 7d: at the end of a series of short-term hydrogenations.

nucleation sites on the surface of particles seem to increase (less and less spherical zones of MgH_2 with deep penetration in the interior of the particle, all around uniform depths of the hydride shell). Fig. 7a and d are representative for hydrogenations resulting from a low and high number of nucleation sites, respectively. Returning to long-term hydrogenation conditions (Fig. 4a) results in a sudden increase in H_2 capacity up to the original value (5.5 wt.%), and the LM image of the hydrogenated material looks at this point like that in Fig. 7b.

On the other hand, the undoped Mg powder (Fig. 4a; cycles number 42–64) shows, under the short-term hydrogenation conditions, no such losses in H_2 capacity, but the increase in hydrogenation pressure from 25 to 35 bar even causes a little increase in capacity (from 5.7 to 6.0 wt.%) [14].

Based upon literature studies [36–44] and our own results (Fig. 7) [14] on hydrogenation of pure [14,36–41] as well as of Ni-doped magnesium [14,42–44], it can be assumed that the observed reversible capacity losses of Ni-doped Mg– MgH_2 materials (Figs. 3, 4), under conditions of the survey test, are caused by an increasing

formation rate of nucleation sites. As mentioned above, the increased number of nucleation sites leads to a premature formation of a dense MgH_2 layer which cuts off further admission of hydrogen. It must, therefore, be realized that the formation of nucleation sites on the surface of Ni-doped Mg particles, in comparison to undoped ones, is extremely favored. Since under short-term (high-pressure) hydrogenation conditions the H_2 -capacity steadily decreases (Fig. 4a, cycle number 1–21), the number of nucleation sites per particle for each new cycle should accordingly *accumulate*. In accordance with the behavior pattern of *pure Mg* [38,40], under long-term (low-pressure) hydrogenation, a lower number of nucleation sites are formed and, owing to this fact, higher hydrogen capacities are achieved.

3.5. High temperature cycling tests

For the comparison of storage properties of different Mg materials under high temperature operational conditions the following materials were chosen: Two commercial Mg powder samples of different origins (Norsk Hydro (NH)

sample and an Eckart–Werke PK-31, 270 mesh sample), a Mg powder produced by spraying melted Mg into an argon atmosphere (Eckart–Werke), a very fine Mg powder (325 mesh, Alpha Products) and the Ni-doped standard material (Section 3.1). The particle size distribution of Mg powders used, as determined by sieving, is shown in Fig. 8. In contrast to Mg flakes prepared by shaving (Fig. 6a), the particles of sprayed Mg have globular shapes.

In the first series of HT cycling tests (Fig. 9a and Fig. 5, □—□), after the first hydrogenation (35 bar/350°C), the (initial) hydrogenation pressures were raised stepwise from 55 to 100 bar, whereby 30–60 cycles were conducted on each of the levels. In the second series (Fig. 9b), 80–100 cycles each were conducted at hydrogenation pressures and oven temperatures ranging from 100–140 bars/470–515°C. The temperature of the autoclaves was alternated hourly between the hydrogen absorption and desorption temperature (Fig. 9c, d). During the HT cycling tests, hydrogenation times were occasionally extended up to the time when the hydrogen uptake completely stopped (up to 15 h); the corresponding cycles appear in Fig. 9a,b as isolated peaks. The H₂-capacity values thus obtained provide information about the maximum storage capacity as attainable under the respective conditions, independent of the usually limited hydrogenation time (1 h).

The dependence of the hydrogen storage capacities upon the number of cycles of the investigated materials is represented in Fig. 9a,b; in Fig. 9c,d are reproduced the charts of oven temperature and pressure changes taking place during each one of the typical cycles of the first and second series of HT cyclic tests.

Under the conditions of the present HT cycling tests, the best results are obviously achieved with the NH sample (Fig. 9a,b, —■—) followed by the 325 mesh Mg powder (—○—). The PK-31 powder showed, under almost identical conditions, a behavior pattern very similar to that of the 325 mesh powder [14]. The sprayed Mg powder and Ni-doped standard material (+++, —▲—), cannot be considered to serve as materials for heat storage under the given HT cycling conditions due to their massive loss in storage capacity.

During the first series of HT tests, the NH Mg-powder showed, at hydrogenation pressures of 85 or 100 bar (Fig. 9a, ■), a cyclic stability in a course of >200 cycles with a storage capacity of 5 wt.% of H₂, corresponding to a heat output per cycle of 0.56 kWh/kg Mg. The chart (Fig. 9c) demonstrates, especially with respect to the NH sample, that both the hydrogenation and the dehydrogenation processes are not completed within the time period allotted to them (1 h). Indeed, a prolongation to 15 h hydrogenation time (cycle no. 315) causes the storage capacity to increase to 6.4 wt.% H₂ (equivalent to 0.76 kWh/kg Mg). According to recent measurements (Fig. 5 and Ref. [16]), the 85 and 100 bar hydrogen pressures correspond to Mg–MgH₂ equilibrium temperatures of 490 and 502°C, respectively. In the case that the thermochemically stored heat is withdrawn from the heat store at such a rate that the temperature in the hydride bed is maintained closely to the hydrogen pressure dependent equilibrium temperature [16], the temperature of the heat delivery of the store is nearly equal to the equilibrium temperature of the applied hydrogen pressure (here 490 or 502°C). As demonstrated in Fig.

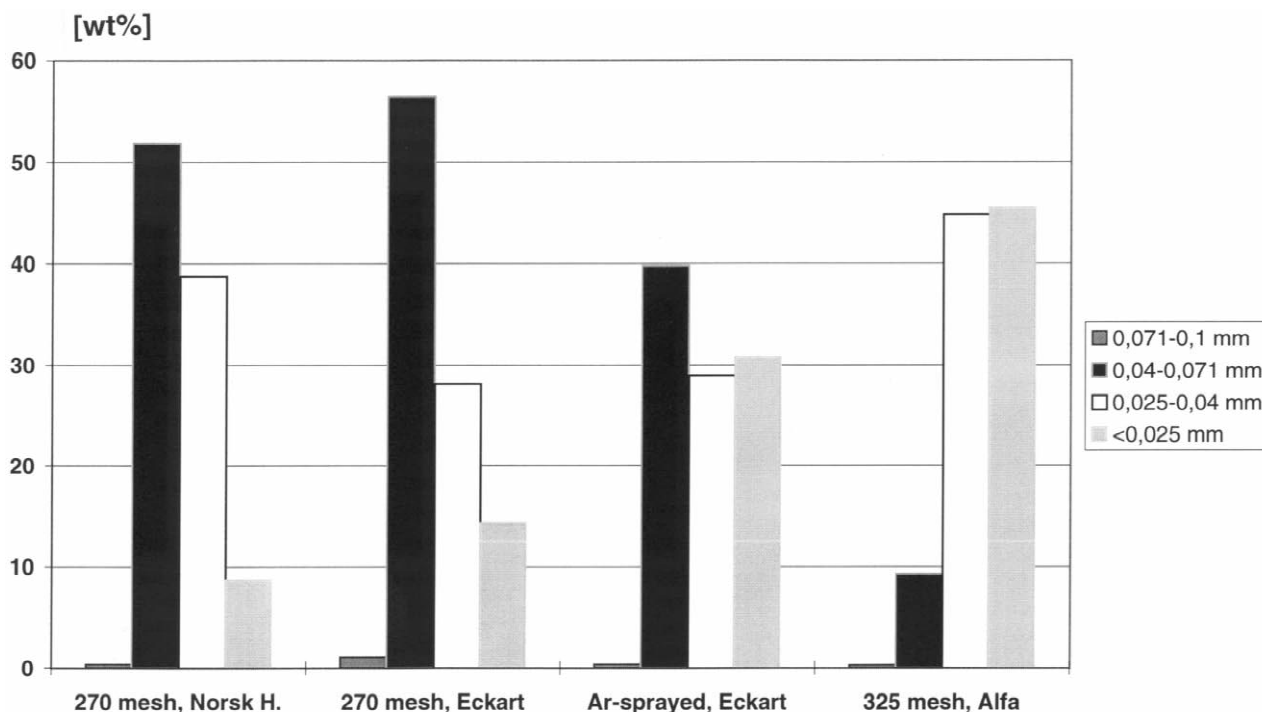


Fig. 8. Particle size distribution of Mg powders applied in high temperature cycling tests.

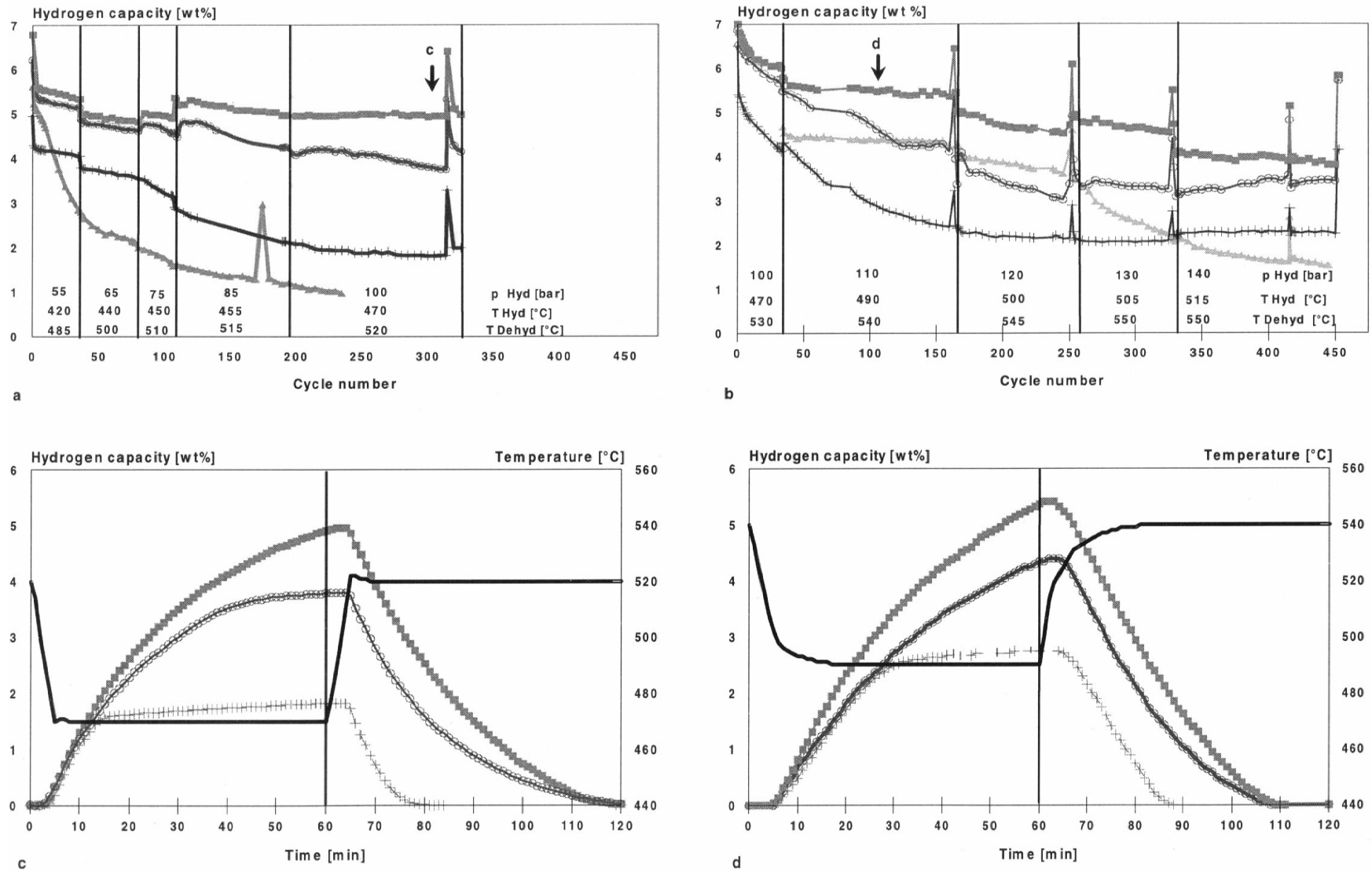


Fig. 9. First (a) and second (b) series of high temperature cycle tests performed with NH (—■—), 325 mesh (—○—) and Ar sprayed Mg powder (++) and with the standard material (—▲—); 1 wt.% of hydrogen capacity in (a) and (b) correspond to drops in hydrogen pressure in the system of 4.0 and 2.0 bar, respectively; the course of hydrogenation/dehydrogenation processes of Mg–MgH₂ samples pertaining to the cycles marked with ↓ are reproduced in (c) and (d); (c) cycle no. 306 in (a); cycle no. 114 in (b); —, oven temperature.

10b (see also Refs. [1,2]), this situation can indeed be realized.

In the second series of the HT cycling tests (Fig. 9b), applying after cycle no. 35 a hydrogenation pressure of 110 bar, the storage capacity of the NH Mg powder slightly decreased from 5.5 to 5.3 wt.% H_2 in the course of ~ 130 cycles (heat output capacities per cycle 0.65–0.63 kWh/kg Mg). Again, the chart (Fig. 9d) shows the incomplete course of the characteristic hydrogenation–dehydrogenation processes and a prolongation of the hydrogenation time (cycle no.: 163, 15 h) results again (see

above) in an increase in storage capacity to 6.4 wt.% H_2 . The hydrogenation pressure of 110 bar, corresponding to the maximum temperature of heat delivery of 508°C (Fig. 5) [17] seems to be the upper limit of cyclic stability conditions of the present material, since a further increase in hydrogenation pressure to 120–140 bar (Fig. 9b) leads to a decrease in cycling stability and a drop in storage capacity to 4.5–4 wt.% H_2 .

In the third series of HT cycling tests, in addition to the NH sample, a coarse (0.071–0.1 mm) and a fine sieving fraction (0.025–0.04 mm; Fig. 8) were simultaneously

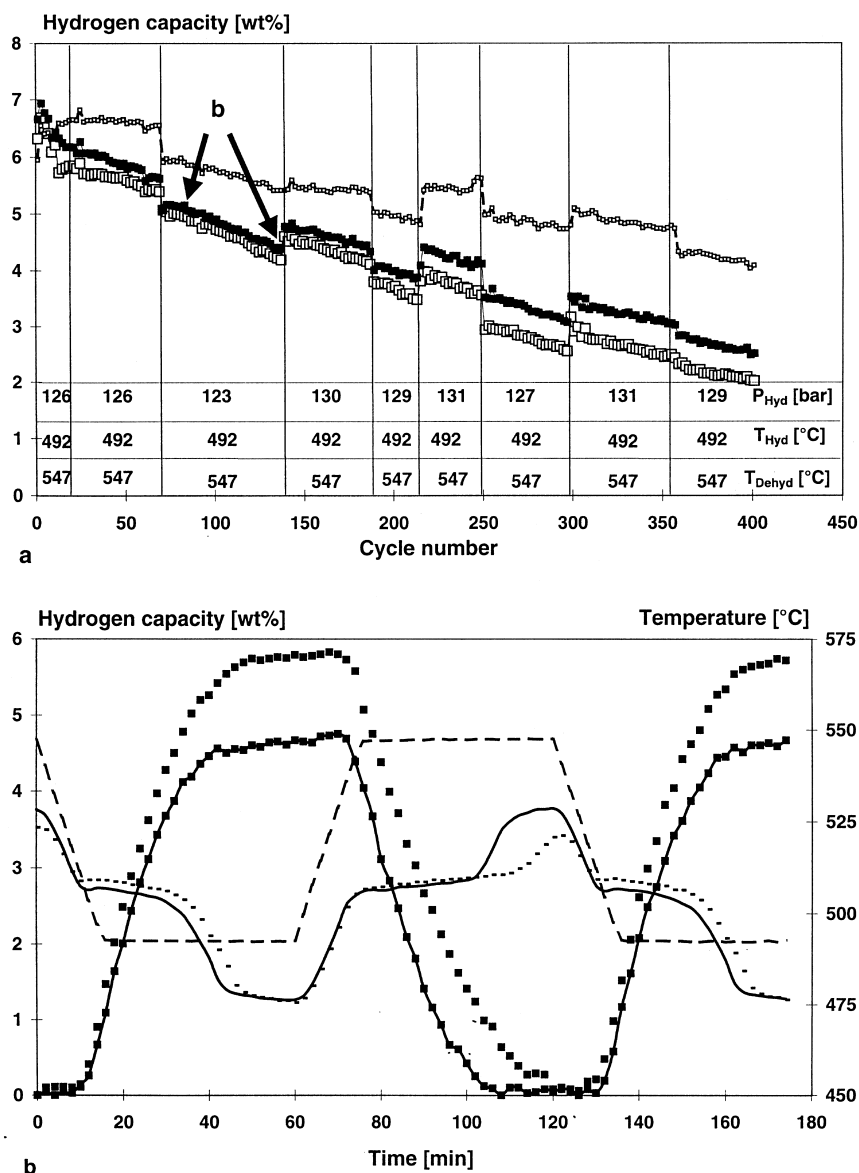


Fig. 10. (a) Third series of high temperature cycle tests performed simultaneously with NH powder (—■—) and with the 0.071–0.1 mm (---□---) and the 0.025–0.04 mm (····□····) sieving fraction thereof; p_{Hyd} , initial hydrogenation pressure; T_{Hyd} , hydrogenation (oven) temperature; T_{Deh} , dehydrogenation (oven) temperature; time allotted for hydrogenation and dehydrogenation, 1 h each; 1 wt.% of hydrogen capacity in Fig. 10 corresponds to a drop in hydrogen pressure in the system of 1.24 bar; the course of the hydrogenation/dehydrogenation processes of the NH sample, together with the inner temperature of the sample, pertaining to the cycles marked with ↓ are reproduced in (b); (b) ■, —■—, hydrogen capacities (in wt.% H_2) of the NH sample as a function of the oven temperature (—) and time, for cycles no. 80 and 140 in (a) (marked with ↓), respectively; ---, —, inner temperature of the NH sample during cycles no. 80 and 140, respectively.

subjected to the cycling test (Fig. 10a and Fig. 5, $\triangle$ — $\triangle$). The cycling conditions (126 bar/492–547°C) were close to those of the second series HT test after cycle 170 (Fig. 9b; 120 bar/500–545°C) which are already conditions of cyclic instability. During the first 71 cycles of the test (Fig. 10a), all three samples revealed a considerable decrease in storage capacity, which became even more pronounced after cycle no. 71, when the samples in dehydrogenated state, were exposed for 1 h to a high temperature (547°C) [9]. This behavior again points towards sintering of the Mg particles (cf. Section 3.4.2) as the cause for cyclic instability under these severe cyclic conditions. Among the three samples investigated, the fine sieved fraction of the NH powder (Fig. 10a, — $\square$ —) displays throughout the test the least loss in storage capacity and should accordingly be considered ahead of NH powder as a Mg–MgH₂ heat storage material under severe operational conditions.

During the third series of the HT cycling tests (Fig. 10a), in addition to the oven temperature and H₂ pressure, the temperature *inside* the Mg–MgH₂ samples could be monitored via thermocouples inserted in the hydride beds (see expt. part). In Fig. 10b, pertaining to the cycles 80 and 140 of the genuine NH sample (marked by an $\downarrow$ in Fig. 10a), temperature changes inside the hydride bed (---, —) together with the corresponding pressure changes in the system, expressed in terms of wt.% H₂ (■, —■—), are plotted against time. From the course of pressure changes it becomes evident that under the present severe conditions (123 bar/492–547°C) the hydrogenation/dehydrogenation processes are more rapid than under the conditions of cyclic stability of the NH sample (Fig. 9c,d). This has the consequence that for about 15 min the sample (Fig. 10b, cycle no. 140) in the dehydrogenated state, is exposed to ~530°C. As mentioned above, this circumstance promotes the sintering process and leads to a diminishing storage capacity. The progress of the sintering process is also recognizable through the increasing inner temperature of the sample in dehydrogenated state with growing number of cycles (Fig. 10b, — versus ---), because sintering increases the heat conductivity of Mg particles. Finally it should be noted that, in the course of hydrogenation or dehydrogenation processes, the temperature inside the sample (Fig. 10b, ---, —) for a while remains at a temperature plateau which, as shown below, roughly corresponds to the equilibrium temperature of the prevailing hydrogen pressure in the system. In Fig. 10b, the plateaus are located at ~505°C. According to Fig. 5 and Ref. [16], the equilibrium H₂ pressure corresponding to the temperature of 505°C amounts to 105 bar. This means that, under the present cycling conditions, heat delivery temperatures of the heat store reaching 505°C, can be attained.

In summary, the performed HT cycle tests demonstrate for the first time that by using a neat Mg powder produced by brushing (Fig. 6a), or particular grain size fractions thereof, and their reversible reaction with hydrogen under pressure (up to ~110 bar), heat storage systems with satisfactory cycling stability operating at a heat delivery

temperature level reaching 500°C (or slightly above, such as 505°C), and with heat storage capacities amounting to 0.6–0.7 kWh/kg Mg, are feasible.

4. Conclusion and outlook

Abundant experimental evidence is presented which indicates that properties of various Ni-doped or undoped Mg–MgH₂ systems to be utilized as heat or hydrogen storage materials (their hydrogen storage capacity, hydrogenation/dehydrogenation rates and cyclic stability) are sensitively dependent upon all the details of experimental cycling conditions. Not only hydrogenation/dehydrogenation pressure and temperature, or rather their “remoteness from the equilibrium conditions” (the thermodynamic driving force), but also the time allotted for hydrogenation/dehydrogenation processes, and the temperature regime of heating and cooling must be specified in order to obtain reproducible results; also, the previous “cyclization history” of a material sample (accumulation effect, Section 3.4.2) has to be taken into account. Even slight deviations from already tested stable cycling conditions can result in serious detrimental effects, especially for the cyclic stability (Sections 3.4, 3.5).

Ni-doped materials have excellent cyclic stability and high hydrogenation/dehydrogenation rates even under very mild pressure/temperature cycling conditions (standard cycling conditions or below [1,2]) suitable for applications such as solar generation of heat and cold [22], heat pumps [10–13], hydrogen storage [3–7] and the like.

On the other hand, based on their cyclic stability and adequate reaction rates under severe reaction conditions, neat Mg powders can be used as cheap materials for reversible thermochemical high temperature heat storage in the temperature range of 450–500°C (H₂ pressures up to 100–110 bar, heat storage capacities 0.6–0.7 kWh/kg Mg) applicable, for example, for solar power generation via Stirling engines [12,13] or storage of industrial heat in this temperature range [15].

For preparing both the Ni-doped and undoped Mg–MgH₂ systems, Mg flakes of a specified particle size distribution (Section 3.5, Fig. 8), produced by brushing of Mg ingots (not sprayed Mg powder), are the materials of choice.

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